NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 3148

EVALUATION OF ALLOYS FOR VACUUM BRAZING OF SINTERED WROUGHT MOLYBDENUM FOR ELEVATED-TEMPERATURE APPLICATIONS

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SUMMARY

In a search for potential brazing alloys for molybdenum for use at elevated temperatures, 25 binary and ternary alloys, with liquidus temperatures in the range 2000° to 2500° F, were prepared and evaluated. Three commercial alloys were also evaluated. The brazing characteristics were established in vacuum.

The room-temperature tensile strengths of butt-brazed molybdenum joints of the 13 alloys having the most promising brazing characteristics ranged from 8450 to 49,400 pounds per square inch. The 10 alloys which possessed room-temperature strengths higher than 21,000 pounds per square inch were tested at 1800° F. At this temperature, strengths varied from 0 to 18,900 pounds per square inch.

The three alloys which had 1800° F bonding strengths of 17,000 to 19,000 pounds per square inch were considered satisfactory and were heated at 1800° F in vacuum for 24 hours to determine the extent of diffusion and the effect on tensile strength. The 84 percent nickel - 16 percent titanium and the 52 percent niobium - 48 percent nickel alloy bonds seemed unaffected by a time of 24 hours at temperature; therefore, these two binary alloys may be potentially useful brazing alloys for molybdenum for elevated-temperature applications. The time at temperature, however, was detrimental to the 50 percent iron - 50 percent palladium alloy since the 1800° F strength dropped from 17,000 to 7000 pounds per square inch.

INTRODUCTION

The many research data published in the last several years on the properties of molybdenum definitely show that this high-melting-point metal has an excellent potentiality for high-temperature applications

in the range of 1800° to 2000° F. Molybdenum, however, has two very undesirable characteristics, namely, poor oxidation resistance above 1000° F and difficult joining properties.

Considerable data exist in the literature on the joining of 3175
molybdenum by several welding methods. In general, most welds made were unsatisfactory because of porosity, cracks, or impurities in the weld and particularly because of recrystallization in the heat-affected zone, all of which can contribute to the embrittlement of the metal. Occasionally, ductile recrystallized welds can be made, but these have not been duplicated consistently. Recrystallization during welding is also detrimental in that recrystallized metal does not possess the superior strength of swaged metal. Therefore, the joining of molybdenum by welding cannot be considered as practical for load-bearing applications at the present stage of development.

A survey of the literature indicates that little development work has been done on the joining of molybdenum by brazing with high-temperature alloys. Interest in this joining method, however, is increasing. In reference 1, a limited amount of encouraging data was recently published on the brazing of molybdenum with a few commercial and other high-temperature alloys having liquidus temperatures in the range 2200° to 2700° F. Although at these temperatures damaging recrystallization occurred, this obstacle can be overcome by controlling the swaging procedures during the fabrication of the molybdenum. References 2 and 3 show that by this method molybdenum can be produced with a recrystallization temperature of 2500° F or higher. Therefore, it is entirely logical that an alloy can be developed which would braze below the recrystallization temperature of the molybdenum and would produce a brazed joint having satisfactory mechanical properties at both room and elevated temperatures. A program was therefore initiated at the NACA Lewis laboratory to develop a satisfactory brazing alloy for molybdenum. The program included:

(1) Fabrication of binary and ternary alloys with liquidus temperatures in the range of approximately 2000° to 2500° F

(2) Evaluation of the brazing characteristics of these alloys with molybdenum in vacuum

(3) Determination of tensile strengths of butt-brazed molybdenum joints at room temperature and 1800° F

DESCRIPTION OF APPARATUS

Vacuum furnace. - Brazing was done in a $1\frac{3}{4}$-inch-diameter zirconium silicate tube which was heated by a Globar furnace. The vacuum system had sufficient pumping capacity to maintain a pressure of less than 0.3 micron at all temperatures, which was adequate to prevent oxidation during brazing.

Brazing assembly. - Figure 1(a) shows an enlarged cross-sectional view of the butt-joint brazing assembly fabricated from sintered wrought molybdenum bar stock, approximately 5/8 inch in diameter. The two male components were made slightly oversize to form a press fit with the female to ensure the retention of the 0.0015±0.0005-inch brazing gap during the brazing cycle. The butt-brazing surfaces were ground to a finish of 5 to 16 rms.

Tensile specimens. - The conical-end, 0.250±0.003-inch-diameter butt-brazed tensile specimens, shown in figure 1(b), were machined from the brazing assembly and the test section surface-ground to 5 to 16 rms.

Tensile-testing machine. - A commercial hydraulic-type tensile machine with a low scale of 6000-pound load capacity was used to evaluate the strength of brazed joints. A loading rate of approximately 10,000 pounds per square inch per minute was employed.

Tensile testing furnace. - The elevated-temperature furnace, gripping mechanism, instrumentation, and oxidation-protection system are detailed in reference 4.

PROCEDURE

Brazing alloy preparation. - Small charges (10 to 100 g) of alloys were prepared from either solid or powdered metal by induction heating in zircon crucibles with a protective layer of argon gas above the charge. Those alloys prepared which showed evidence of contamination or had a weight loss or gain in excess of 5 percent were considered unsatisfactory and discarded.

Brazing. - All alloys were first evaluated as to their ability to wet molybdenum in vacuum. Small quantities of brazing materials were placed in molybdenum cups, made from the same 5/8-inch swaged bar stock used for tensile specimens, and heated in vacuum to a temperature of $100^{\circ} \pm 50^{\circ}$ F above the liquidus temperature of the brazing alloys. To prevent any oxidation, all brazing cycles were begun in a cold evacuated furnace; a heating time of $2\frac{1}{2}$ to $3\frac{1}{2}$ hours was required to attain the melting temperature. The samples were then furnace-cooled to room temperature. Polished cross sections of the brazed cups were examined with a metalloscope to evaluate the brazing

characteristics of the alloys. Butt-brazed tensile specimens, made with the 13 alloys having the most desirable wetting characteristics, were brazed in an identical manner.

Tensile-strength evaluation. - A nearly constant loading rate of 10,000 pounds per square inch was maintained up to the occurrence of failure during both room-temperature and 1800° F testing. The heating cycle for the 1800° F tests was 1.5 hours to temperature plus a 15-minute soak at 1800° F. 3175

Metallography. - The metallographic techniques used for the molybdenum are detailed in reference 4. Additional etchants were required to reveal the microstructure of the brazed joints. A 5 percent sodium hydroxide - 15 percent potassium ferricyanide etchant solution was used for the photomicrographs.

RESULTS AND DISCUSSION

Brazing alloys. - Table I lists three commercial alloys and the nominal composition of the 25 brazing alloys which were successfully prepared in zircon crucibles. The melting points or ranges were determined from equilibrium diagrams in the literature. Hardness values of the brazing alloys were obtained with a Tukon hardness tester and converted from Knoop values to Rockwell C numbers.

The fractured surfaces of all the alloys appeared to be homogeneous and oxide-free when examined under a magnification of 15. Since the weight change was 2 percent or less during alloying and the fractures appeared satisfactory, it is believed that the actual percentage compositions are close to the intended compositions. The liquidus temperatures are therefore probably within a few degrees of those reported.

Brazing characteristics. - The brazing characteristics of the alloys were evaluated from polished and etched cross sections of small molybdenum cups in which the alloys had been melted. Table I lists a brazing rating of either excellent, good, fair, or unsatisfactory and also remarks for each alloy. This evaluation was based primarily on the ability of the braze to wet the base metal. Secondary considerations were the presence of porosity, cracks, voids, or oxides in the braze, the hardness of the braze, and the tendency to cause intergranular corrosion of the molybdenum.

The vacuum obtained during brazing appeared to be adequate to prevent surface oxidation of the molybdenum and all of the alloys except the 84 percent Ni - 16 percent Ti alloy. The surface of this

braze material and also the adjacent molybdenum surface was a blue-to-purple color after brazing, which is the characteristic color of some oxides of titanium. This coating, however, appeared only on the exposed surfaces. There was no evidence of such an oxide layer between the braze and the molybdenum which would interfere with forming a bond.

Ultimate tensile strength of butt-brazed joints at room temperature and 1800° F. - Butt-brazed tensile specimens were fabricated with
3175 all the alloys which had been given a brazing rating of excellent or good and with the two best alloys rated as fair. Table II lists the tensile strength of the brazed joints at room temperature, at 1800° F, and at both temperatures for three potentially useful alloys which were given a high-temperature diffusion treatment for possible improvement in tensile strength. All strength values reported herein are approximately true brazing bond strengths, since all tensile specimens failed partly or completely through the cross section of the brazed joint.

As-brazed room-temperature tensile strengths ranged from 8450 to 49,400 pounds per square inch. The three alloys having strengths less than 21,000 pounds per square inch were not investigated further. The as-brazed strength of the others at 1800° F varied from 0 to 18,900 pounds per square inch. Those possessing an 1800° F strength of less than 15,000 pounds per square inch were considered unsatisfactory for elevated-temperature use; therefore, all but the following three brazing alloys were eliminated: 84 percent Ni - 16 percent Ti; 52 percent Nb - 48 percent Ni; and 50 percent Fe - 50 percent Pd. Brazed specimens of these three alloys were heated at 1800° F for 24 hours in vacuum to determine the extent of diffusion and the effect on tensile strength.

The 84 percent Ni - 16 percent Ti alloy bond had excellent strength (approx. 18,000 psi) at 1800° F; however, the comparative room-temperature strength (27,000 psi) was rather low. There is no apparent reason for this, since the brazing alloy did not seem brittle and had a hardness of Rockwell C-33. There could, however, have been a very thin interface layer between the braze and the molybdenum, composed of all three elements, which could account for the low room-temperature strength. Comparison of the photomicrographs in figure 2 shows that a 24-hour heating period at 1800° F is not sufficient time nor temperature to form a diffusion layer between the brazing alloy and the molybdenum which could change the properties of the brazed joint. Evidently no physical change occurred, since the strength at both room temperature and 1800° F remained approximately unchanged after this heat treatment.

The 52 percent Nb - 48 percent Ni alloy bond also had a high tensile strength (19,000 psi) at 1800° F and a very low (22,000 psi) comparative room-temperature strength. This is probably due to the brittleness of the brazing alloy which had a hardness of Rockwell C-63. The addition of a small amount of another element to decrease this hardness would probably result in a much higher room-temperature strength without appreciably lowering the 1800° F strength. Figure 3 shows that the 24-hour heating at 1800° F increased the diffusion layer between the braze and the base metal. Although this physical change occurred on heating, it did not affect the tensile strength at 1800° F. At room temperature, two values (25,000 and 40,000 psi) were obtained which are higher than the value of 22,000 pounds per square inch before heat treating. This increase could be attributed to the diffusion treatment, but is believed to be within the normal scatter to be expected in the evaluation of a brittle brazing material.

The 50 percent Fe - 50 percent Pd alloy had an 1800° F strength of 17,300 pounds per square inch and a higher (49,000 psi) comparative room-temperature strength than either the 84 percent Ni - 16 percent Ti or the 52 percent Nb - 48 percent Ni alloy. This strength superiority, however, was lost when the brazed joints were given the 24-hour diffusion treatment at 1800° F. The room-temperature strength was only reduced to 42,000 pounds per square inch but the 1800° F strength dropped from 17,300 to approximately 7000 pounds per square inch. The photomicrographs of figure 4 show two entirely different braze structures, but this difference cannot be attributed to the diffusion treatment since another duplicate specimen also heated 24 hours at 1800° F had a physical appearance similar to the as-brazed structure (fig. 4(a)). Strength cannot be correlated with physical appearance of the brazed joint since both types had a low strength (7000 psi) after heating. It is quite definite, though, that time at 1800° F has a deleterious effect upon the elevated-temperature strength of the 50 percent Fe - 50 percent Pd alloy joint.

SUMMARY OF RESULTS

The following results were obtained in an investigation of new potential brazing alloys for joining molybdenum:

1. A total of 25 binary and ternary alloys with liquidus temperatures in the range of 2000° to 2500° F were prepared. The brazing characteristics of the 25 alloys plus three commercial alloys were evaluated in vacuum and given a qualitative brazing rating.

2. The room-temperature tensile strengths of butt-brazed molybdenum joints for all the alloys rated as excellent and good and for two rated as fair ranged from 8450 to 49,400 pounds per square inch.

3. The tensile strength of the 10 alloys which had room-temperature strengths above 21,000 pounds per square inch varied from 0 to 18,900 pounds per square inch when the test temperature was raised to 1800° F.

3175 4. The three alloys (84 percent Ni - 16 percent Ti; 52 percent Nb - 48 percent Ni; 50 percent Fe - 50 percent Pd) which possessed superior 1800° F joint strengths of 17,000 to 19,000 pounds per square inch were heated for 24 hours at 1800° F in vacuum to determine the extent of diffusion and the effect on tensile strength. The 84 percent Ni - 16 percent Ti and the 52 percent Nb - 48 percent Ni alloy bonds seemed unaffected by heating at 1800° F for 24 hours. These two alloys therefore are potentially useful as brazing alloys for molybdenum for high-temperature service.

5. The 50 percent Fe - 50 percent Pd alloy was materially affected by the 24-hour diffusion treatment. The time at temperature lowered the 1800° F strength from 17,300 to approximately 7000 pounds per square inch, which would therefore make the brazed joint unsatisfactory for 1800° F applications.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, March 16, 1954

REFERENCES

1. Jacobson, M. I., Martin, D. C., and Voldrich, C. B.: Production of Sound Ductile Joints in Molybdenum. Quarterly Prog. Rep., Battelle Memorial Inst., July 17, 1953. (Contract No. AF 33(616)-10, E.O. No. R446-48 SA-18.)

2. Dike, Kenneth C., and Long, Roger A.: Effect of Prestraining on Recrystallization Temperature and Mechanical Properties of Commercial, Sintered, Wrought Molybdenum. NACA TN 2973, 1953.

3. Bechtold, J. H.: Recrystallization Data Applied to Control of the Mechanical Properties of Molybdenum. Scientific Paper 1696, Westinghouse Res. Labs., East Pittsburgh (Pa.), Oct. 28, 1952.

4. Long, R. A., Dike, K. C., and Bear, H. R.: Some Properties of High-Purity Sintered Wrought Molybdenum Metal at Temperatures up to 2400° F. NACA TN 2319, 1951.

TABLE I. - BRAZING CHARACTERISTICS OF ALLOYS MELTED IN VACUUM ON MOLYBDENUM

Nominal composition, percent	Melting range, °F	Hardness, Rockwell C	Brazing rating, based primarily on wettability	Remarks
50 Fe, 50 Pd	2375-2400	8	Excellent	---
60 Pd, 40 Cu	2200-2225	25		(a)
52 Nb, 48 Ni	2175	63		(b)
80 Ni, 20 Mn	2200-2300	52		---
84 Ni, 16 Ti	2350	33		(c)
70 Pd, 30 Cu	2350-2375	Very soft	Good	---
80 Pd, 20 Co	2375-2400	Very soft		(b)
80 Pd, 20 Ni	2375-2400	3		(c)
60 Pd, 40 Ni	2250	7		(b)
70 Pd, 30 Fe	2400	22		(b)
76 Ni, 24 Nb	2325	51		(a)
40 Au, 40 Ag, 20 Pd	2210	Very soft	Fair	(a,b)
60 Pt, 40 Cu	2425-2525	10		(d)
87 Fe, 13 Ti	2375	24		---
84 Fe, 16 Zr	2425	40		(b)
50 Pd, 50 Ag	2350-2450	16		(a)
50 Ni, 50 Sn	2150-2250	60		(a,b)
58 Fe, 42 Al	2250	56		(e)
Hastelloy B	2410-2460	58		(a,b)
50 Fe, 50 Si	2300	--	Unsatisfactory	(f,g)
60 Mn, 40 Fe	2400	--		(f)
65 Cu, 35 Ni	2175-2300	--		(f,h)
52 Cr, 48 Ni	2450	--		(f)
45 Al, 35 Ni, 20 Cu	2275	--		(e,f)
50 Ni, 40 Cu, 10 Al	2275	--		(f,g)
42 Ni, 38 Fe, 20 Ti	2025	--		(f,g)
Stoody 6	2325	--		(b,f)
Nicrobraz	1850-1900	--		(f)

[a]Some intergranular corrosion of molybdenum.
[b]Some porosity in brazing alloy.
[c]A few large voids in brazing alloy.
[d]Molten braze flowed uphill and would not remain in the 0.0015-in. gap in brazing specimen.
[e]Numerous cracks in brazing alloy.
[f]Brazing alloy essentially nonadherent.
[g]Excessive porosity in brazing alloy.
[h]Oxides in brazing alloy.

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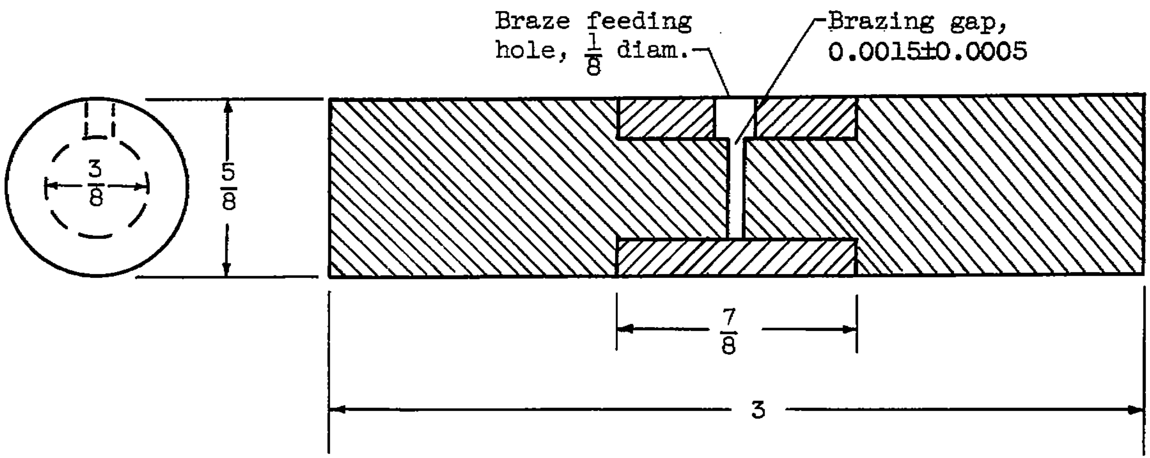
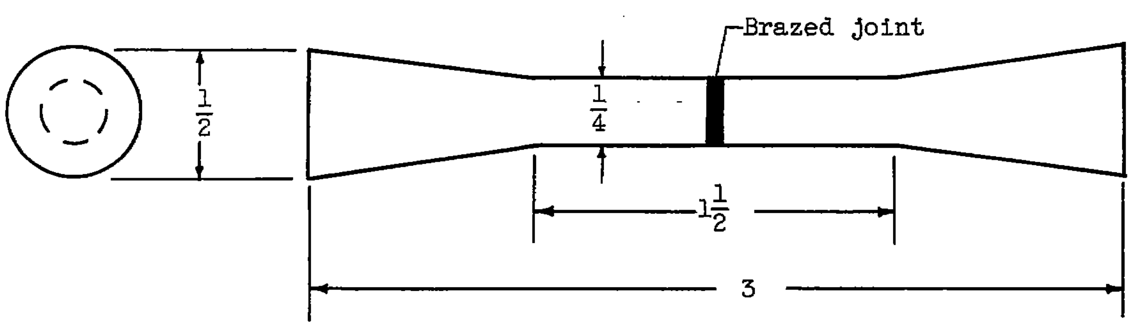
TABLE II. - SHORT-TIME TENSILE STRENGTH OF BRAZED MOLYBDENUM JOINTS

Nominal brazing alloy composition, percent	Testing temperature, °F	Ultimate tensile strength, lb/sq in.	Remarks
84 Ni, 16 Ti	Room	27,800	---
↓	↓	26,200	---
		28,400	(a)
		22,200	(a)
	1800	18,100	---
	↓	17,600	---
		18,300	(a)
		17,300	(a)
52 Nb, 48 Ni	Room	21,700	---
↓	↓	39,700	(a)
		25,500	(a)
	1800	18,900	---
	↓	19,900	(a)
		17,300	(a)
50 Fe, 50 Pd	Room	49,400	---
↓	↓	34,200	(b)
		43,500	(a)
	1800	17,300	---
	↓	7,150	(a)
		6,600	(a)
70 Pd, 30 Cu	Room	42,100	(c)
↓	↓	21,300	---
	1800	8,500	---
60 Pd, 40 Cu	Room	46,100	---
↓	1800	4,650	---
60 Pd, 40 Ni	Room	38,400	---
↓	1800	8,450	---
80 Pd, 20 Ni	Room	31,900	---
↓	1800	0	(d)
76 Ni, 24 Nb	Room	27,400	---
↓	1800	14,200	---
80 Ni, 20 Mn	Room	24,800	---
↓	1800	10,100	---
80 Pd, 20 Co	Room	24,200	---
↓	1800	0	(e)
87 Fe, 13 Ti	Room	20,600	---
84 Fe, 16 Zr	Room	16,400	---
70 Pd, 30 Fe	Room	8,450	---

[a]Heated for 24 hr at 1800° F in vacuum.
[b]Failed through molybdenum.
[c]Estimated, brazed joint thickness of 0.0000 to 0.0002 in.
[d]Failed through joint from weight of grips at about 1500° F.
[e]Failed through joint from weight of grips at about 1600° F.

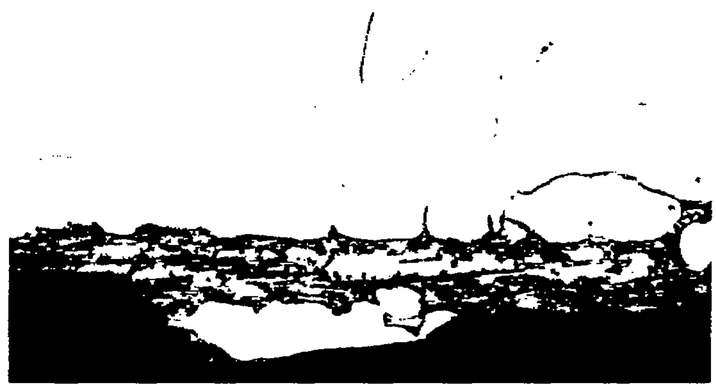


(a) Butt-joint brazing assembly.

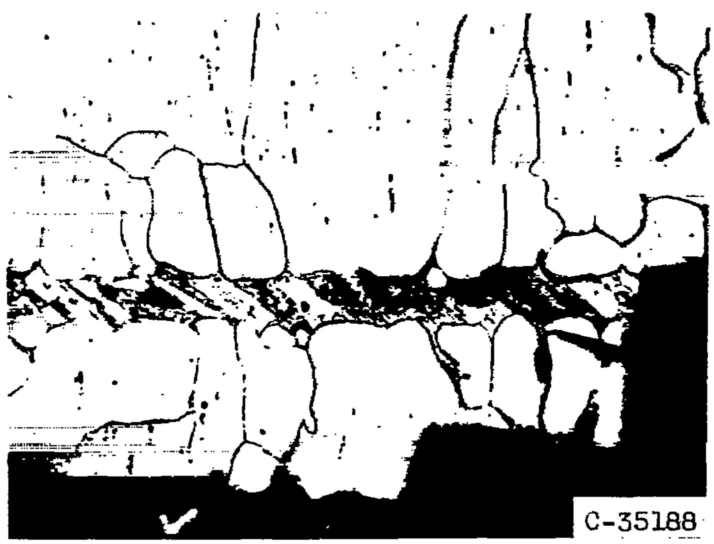


(b) Brazed tensile specimen machined from assembly shown in figure 1(a).

Figure 1. - Molybdenum brazing specimens. (All dimensions are in inches.)

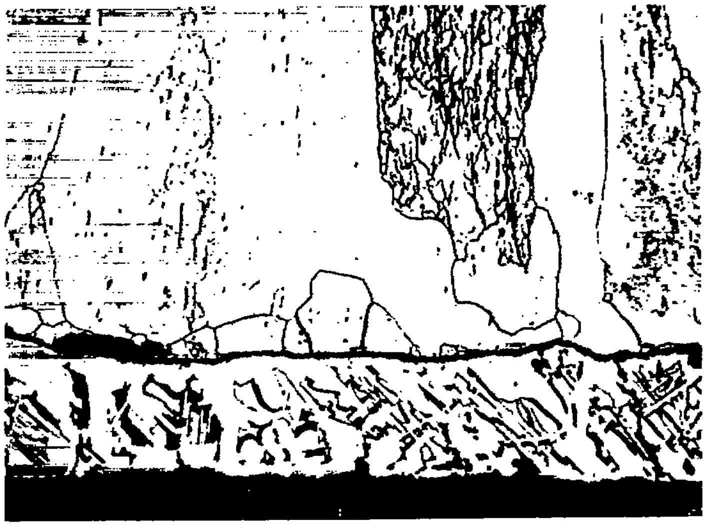


(a) Brazed at 2450° F.



(b) Brazed at 2450° F and soaked for 24 hours at 1800° F.

Figure 2. - Molybdenum vacuum-brazed with 84 percent nickel - 16 percent titanium alloy (fractured joint). X250; caustic cyanide etch.



(a) Brazed at 2300° F.

(b) Brazed at 2300° F and soaked for 24 hours at 1800° F.

Figure 3. - Molybdenum vacuum-brazed with 52 percent niobium - 48 percent nickel alloy (fractured joint). X250; caustic cyanide etch.

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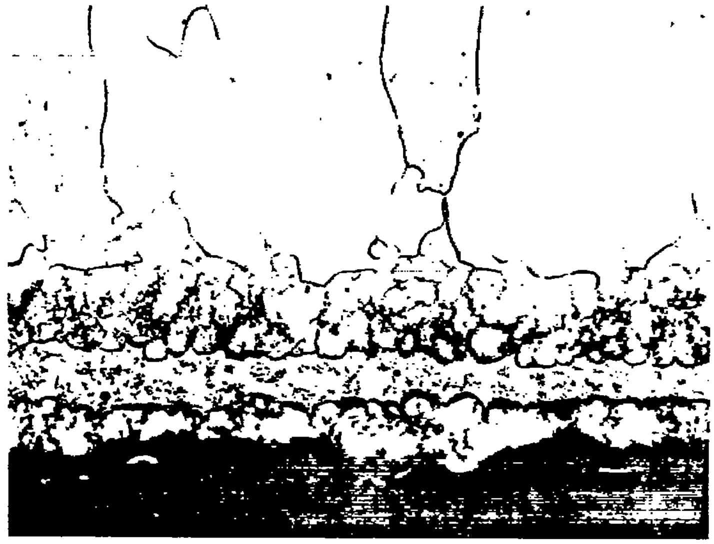

(a) Brazed at 2500° F.

(b) Brazed at 2500° F and soaked for 24 hours at 1800° F.

Figure 4. - Molybdenum vacuum-brazed with 50 percent iron - 50 percent palladium alloy (fractured joint). X250; caustic cyanide etch.